Synthesis of 3,5,5-Trinitropentacyclo[5.3.0.0^{2,6}.0^{3,10}.0^{4,8}]decane

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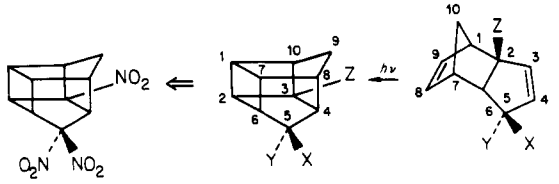
Received December 31, 1983

There is considerable current interest in the synthesis and chemistry of strained energetic compounds.[1-3] Polynitropolycyclic compounds are potential members of this important class. However, very few nitro-containing polycyclic "cage" compounds have been synthesized.[1-3] We now report the synthesis of the title compound (1) in 13 stereocontrolled steps (see Scheme I). To our knowledge, this is the first polynitrobishomocubane to have been synthesized.

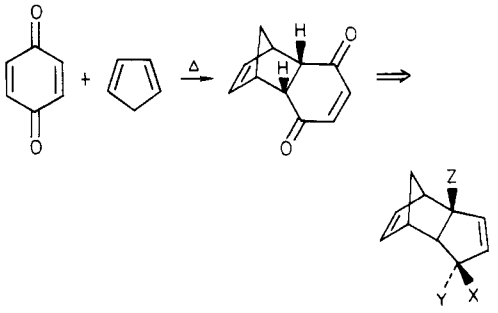
A partial retrosynthetic perspective leading to 1 is shown below.



1

Introduction of the three nitro groups could occur either in an early stage of the synthesis, or, alternatively, the X, Y, and Z substituents could be converted to NO_2 substituents at a later stage, (e.g., after construction of the bishomocubane ring system). Of these two approaches, the latter was preferred. Once the appropriately substituted cage system had been constructed (i.e., 5), we relied on published procedures to effect conversion of the ketone functionality first to a nitro group[4,5] and then to geminal dinitro groups.[6] Subsequent conversion of the carbomethoxyl group in 8 to NO_2 via the sequence shown in Scheme I[7,8] completed the synthesis.

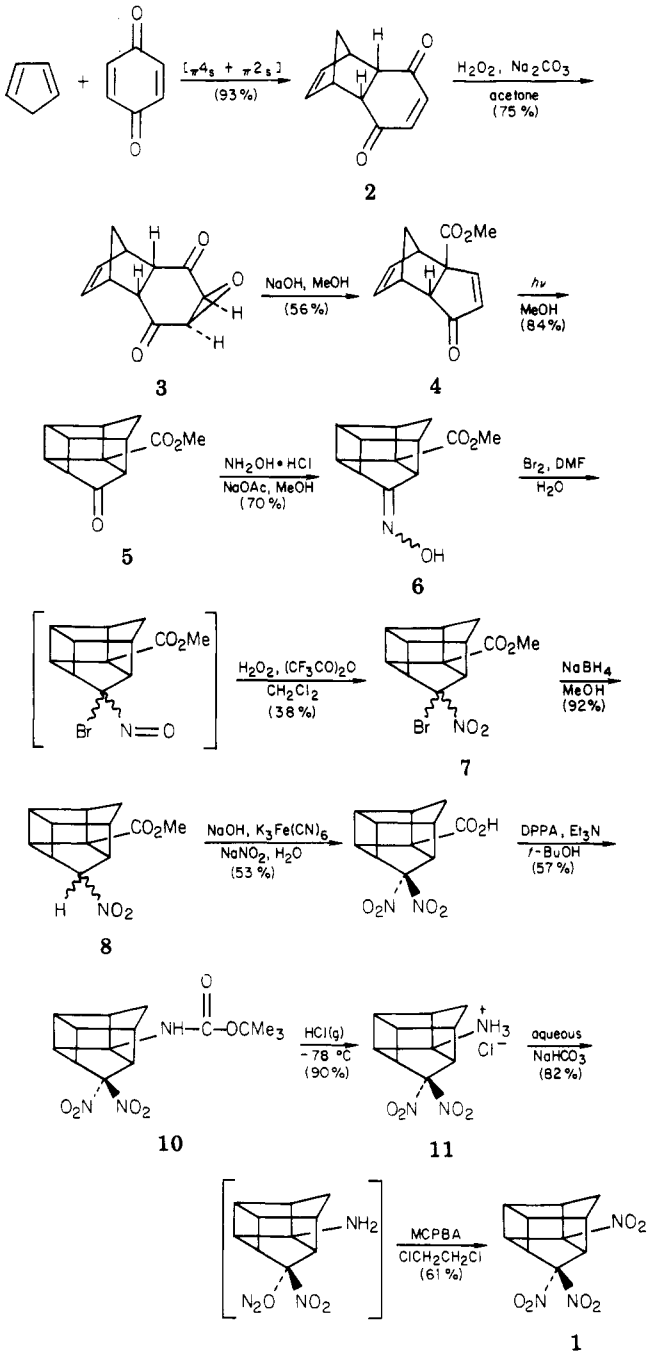
The retrosynthesis of 1 is completed below.



4 (X, Y = carbonyl oxygen; Z = CO_2Me)

The required *exo*-2-carbomethoxytricyclo[5.2.1.0^{2,6}]-deca-3,8-dien-5-one (4) proved to be accessible in good overall yield from readily available, inexpensive starting materials (i.e., cyclopentadiene and *p*-benzoquinone) by using the route indicated in Scheme I.[9-11]

Scheme I



Experimental Section

Melting points and boiling points are uncorrected. Proton NMR spectra (60 MHz) were obtained on a Hitachi-Perkin Elmer Model R-24B NMR spectrometer. ^{13}C NMR spectra were recorded on a JEOL FX-90Q NMR spectrometer. In all cases, signals are reported in parts per million (δ) downfield from internal tetramethylsilane. Infrared spectra were obtained on a Perkin-Elmer Model 1330 infrared spectrophotometer. Mass spectra were obtained on a Hewlett-Packard Model 5970A GC/MS system operating at 70 eV. Elemental microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, TN. Compounds 2[9] and 3[10] were synthesized by literature methods in 93% and 75.5% yield, respectively.

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***exo*-2-Carbomethoxytricyclo[5.2.1.0^{2,6}]deca-3,5-dien-5-one (4).**[11] A saturated solution of sodium hydroxide in methanol was prepared by dissolving sodium hydroxide (25 g) in dry methanol (100 mL); the mixture was allowed to stand at room temperature for 2 days before use. To a warm solution of **3** (10.0 g, 52.6 mmol) in methanol (200 mL) was added saturated methanolic sodium hydroxide solution (3.5 mL). The reaction mixture was stirred at 45 °C for 1 h. The resulting highly colored solution was concentrated under reduced pressure. The viscous residue thereby obtained was diluted with water and then extracted with ether. The organic layer was washed with water until the washings became neutral. The organic layer was then dried (anhydrous Na_2SO_4) and filtered, and the filtrate was concentrated in vacuo to afford a viscous oil (ca. 7 g). This material was adsorbed onto a silica gel column and eluted rapidly with 3% ethyl acetate–hexane solution. The eluate was concentrated and distilled in vacuo to afford **4** (6.0 g, 56%), bp 98 °C (0.1 mm). The distillate was dissolved in hot hexane; when cooled, a colorless microcrystalline solid, mp 65 °C, crystallized from solution: ^{1}H NMR ($CDCl_3$) δ 1.73 (*AB*, J_{AB} = 8.9 Hz, 1 H), 1.96 (*AB*, J_{AB} = 8.9 Hz, 1 H), 3.1–3.4 (m, 3 H), 3.77 (s, 3 H), 5.94 (d, J = 5.7 Hz, 1 H), 5.8–6.1 (m, 2 H), 7.38 (d, J = 5.7 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 45.58 (d), 49.48 (d), 51.10 (t), 52.57 (q), 54.14 (d), 64.16 (s), 133.45 (d), 134.60 (d), 136.00 (d), 161.18 (d), 173.10 (s), 208.00 (s); IR (KBr) 2990 (w), 2960 (w), 1705 (vs), 1690 (vs), 1430 (m), 1220 (s), 1020 (m), 845 (m), 735 (m) cm^{-1}.

Anal. Calcd for $C_{12}H_{12}O_3$: C, 70.57; H, 5.92. Found: C, 70.60; H, 6.19.

3-Carbomethoxypentacyclo[5.3.0.0^{2,6}.0^{3,10}.0^{4,8}]decan-5-one (5). A solution of **4** (13.0 g, 63.7 mmol) in methanol (300 mL) was irradiated for 20 h with a 450-W Hanovia medium-pressure Hg lamp (Pyrex filter). The reaction mixture was then concentrated, and the residue was disilled in vacuo to afford **5**: 11.0 g, 84.4%; bp 85 °C (0.02 mm); ^{1}H NMR ($CDCl_3$) δ 1.65 (*AB*, J_{AB} = 11 Hz, 1 H), 1.93 (ABC, J_{AB} = 11 Hz, J_{BC} = 2.2 Hz, 1 H), 2.4–2.7 (m, 2 H), 2.9–3.2 (m, 4 H), 3.4 (m, 1 H), 3.66 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 36.32 (d), 37.99 (d), 39.89 (d), 40.22 (d), 40.60 (t), 42.76 (d), 46.66 (q), 51.16 (d), 52.57 (d), 53.38 (s), 172.13 (s), 212.87 (s); IR (neat) 2980 (s), 2950 (s), 2860 (w), 1750 (vs), 1715 (vs), 1430 (s), 1315 (s), 1265 (s), 1230 (s), 1150 (m), 940 (m) cm^{-1}.

Anal. Calcd for $C_{12}H_{12}O_3$: C, 70.57; H, 5.92. Found: C, 70.64; H, 6.02.

3-Carbomethoxypentacyclo[5.3.0.0^{2,6}.0^{3,10}.0^{4,8}]decan-5-one Oxime (6).[12] To an ice-cold solution of **5** (10.04 g, 49.22 mmol) in methanol (50 mL) was added sodium acetate (8.8816 g, 108.27 mmol) and hydroxylamine hydrochloride (3.7625 g, 54.137 mmol). The reaction mixture was stirred for 2 h at 0 °C and then diluted with water. The resulting mixture was then extracted with ether. The organic layer was washed successively with water and then with brine, dried (anhydrous sodium sulfate), and filtered, and the filtrate was concentrated in vacuo. The residue was then chromatographed on silica gel (20% ethyl acetate–hexane eluent), affording **6** (mixture of syn and anti oximes, 7.5 g, 70% yield): ^{1}H NMR ($CDCl_3$) δ 1.52 (*AB*, J_{AB} = 9.5 Hz, 1 H), 1.93 (*AB*, J_{AB} = 9.5 Hz, 1 H), 2.6–3.5 (m, 7 H), 3.68, 3.70 (s, carbomethoxyl methyl protons of the syn and anti oxime isomers, 3 H), 8.97 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 55.98, 56.47 (q, carbomethoxyl methyl carbons of the syn and anti oxime isomers), 168.3, 165.8 (s, C_5 of syn and anti oxime isomers), 173.4 (s, carbomethoxyl carbonyl carbon atoms of syn and anti oxime isomers); IR (neat) 3330 (s), 1710 (vs), 1435 (s), 1315 (vs), 1270 (s), 730 (m) cm^{-1}.

Anal. Calcd for $C_{12}H_{13}NO_3$: C, 65.74; H, 5.98; N, 6.39. Found: C, 65.75; H, 6.14; N, 6.10.

3-Carbomethoxy-5-bromo-5-nitropentacyclo[5.3.0.0^{2,6}.0^{3,10}.0^{4,8}]decane (7).[4] To a stirred, ice-cold solution of oxime **6** (8.7082 g, 39.7635 mmol), sodium bicarbonate (8.35 g, 0.10 mol), dimethylformamide (40 mL), and water (200 mL) was added bromine (6.3550 g, 39.7635 mmol) dropwise during 5 min. The mixture was then stirred for an additional 15 min after the bromine addition had been completed. The resulting blue solution was extracted with methylene chloride (3 × 25 mL), and the combined extracts were washed with water, dried (anhydrous sodium sulfate), cooled in a refrigerator for 1 h, and then filtered. The cold filtrate was added dropwise during a 40-min period to a stirred solution of 90% hydrogen peroxide (30 mL) and trifluoroacetic anhydride (16.0 mL) in anhydrous methylene chloride (40 mL) at room temperature. The resulting mixture was concentrated in vacuo. The residue was then diluted with water and extracted with methylene chloride. The organic layer was washed successively with water and with brine, dried (anhydrous sodium sulfate), filtered, and then concentrated in vacuo to afford crude **7** (8.79 g). The crude product was chromatographed on silica gel (5% ethyl acetate–hexane eluent), affording **7** as a mixture of isomers [*exo*-5-bromo-*endo*-5-nitro- and *endo*-5-bromo-*exo*-5-nitro-**7**, ratio (by NMR) 2.8:1, 4.66 g, 38%]; ^{1}H NMR ($CDCl_3$) δ 1.49–2.12 (AB pattern, C_9 protons, 2 H), 2.8–3.6 (m, 7 H), 3.67, 3.75 (s, ester methyl groups of exo-5-bromo-endo-5-nitro and endo-5-bromo-exo-5-nitro isomers, 3 H); IR (neat) 1715 (br, vs), 1535 (br, vs), 1340 (s), 1320 (s) cm^{-1}.

Anal. Calcd for $C_{12}H_{12}BrNO_4$: C, 45.88; H, 3.85. Found: C, 46.08; H, 3.99.

3-Carbomethoxy-5-nitropentacyclo[5.3.0.0^{2,6}.0^{3,10}.0^{4,8}]decane (8).[5] In a 200-mL, two-necked flask fitted with a reflux condenser, a magnetic stirrer, and a dropping funnel was placed a solution of sodium borohydride (2.2445 g, 59.331 mmol) in 75% aqueous methanol (43 mL). To the dropping funnel was added a solution of **7** (4.6575 g, 14.824 mmol) in methanol (4 mL). The methanolic solution of **7** was then added dropwise to the methanolic sodium borohydride solution until the reaction became self-sustaining, at which time the remainder of the methanolic solution of **7** was added rapidly. The resulting mixture was stirred for 15 min, at which time excess dilute, aqueous acetic acid was added to acidify the reaction mixture. The resulting mixture was then concentrated in vacuo, and the residue was diluted with water and extracted with ether. The combined ethereal layers were washed successively with water and then with brine, dried (anhydrous sodium sulfate), and filtered, and the filtrate was concentrated in vacuo to afford crude **8** as a viscous liquid (3.20 g, 91.8%). The crude product was disilled in vacuo (bp 120 °C (0.02 mm)) to afford **8** as a mixture of isomers [*exo*-5-nitro- and *endo*-5-nitro-**8**, ratio (by NMR) 2:1]; ^{1}H NMR ($CDCl_3$) δ 1.2–2.0 (AB pattern C_9 protons, 2 H), 2.8–3.3 (m, 7 H), 3.67, 3.69 (s, carbomethoxyl methyl groups of exo-5-nitro and endo-5-nitro isomers, 3 H), 4.80, 4.87 (m, C_5 protons of exo-5-nitro and endo-5-nitro isomers, 1 H); IR (neat) 2980 (s), 2860 (m), 1710 (br, vs), 1530 (br, vs), 1370 (s), 1320 (s), 1150 (vs), 765 (m) cm^{-1}.

Anal. Calcd for $C_{12}H_{13}NO_4$: C, 61.27; H, 5.57; N, 5.95. Found: C, 61.47; H, 5.48; N, 5.89.

5,5-Dinitropentacyclo[5.3.0.0^{2,6}.0^{3,10}.0^{4,8}]decane-3-carboxylic Acid (9).[6] To a rapidly stirred solution of sodium hydroxide (1.2 g, 0.03 mol) in 38.3% aqueous methanol (65 mL) was added **8** (2.00 g, 8.52 mmol) under a nitrogen blanket. The resulting yellow solution was added dropwise under nitrogen to a vigorously stirred solution of potassium ferricyanide (14.5876 g, 44.521 mmol) and sodium nitrite (6.1136 g, 77.387 mmol) in water (100 mL). The reaction mixture was stirred for 1 h after the addition had been completed. The reaction mixture was then acidified by addition of dilute hydrochloric acid and extracted with ether. The combined ethereal extracts were washed successively with water and with brine, dried (anhydrous sodium sulfate), and filtered, and the filtrate was concentrated in vacuo to afford crude **9**. Recrystallization of this material from 35% ethyl acetate–hexane afforded pure **9**: 1.2 g, 53%; mp 154–155 °C; ^{1}H NMR ($CDCl_3$) δ 1.63 (*AB*, J_{AB} = 12.1 Hz, 1 H), 2.07 (*AB*, J_{AB} = 12.1 Hz, 1 H), 2.8–3.8 (m, 7 H), 11.14 (br s, 1 H); ^{13}C NMR ($CDCl_3$) δ 37.35 (d), 39.00 (d), 39.59 (t), 42.49 (d), 45.85 (d), 46.88 (d, 2 C), 57.22 (d), 57.44 (s), 127.7 (s), 177.7 (s): IR (KBr) 1625 (vs), 1545 (vs), 1320 (s), 1280 (s), 1165 (m), 785 (s), 640 (m) cm^{-1}; mass spectrum (70 eV), *m/e* (relative intensity) (no molecular ion), 128.05 (22.0), 117.05 (15.8), 116.05 (13.0), 114.95 (23.2), 105.05 (16.4), 91.05 (16.4), 77.15 (22.0), 66.05 (48.6), 64.95 (29.9), 62.95 (18.6), 61.85 (15.8), 51.05 (22.6), 50.05 (18.1), 46.95 (15.3), 43.95 (100.0), 41.15 (13.0).

Anal. Calcd for $C_{11}H_{10}N_2O_6$: C, 49.63; H, 3.78. Found: C, 49.70; H, 3.90.

***tert*-Butyl 5,5-Dinitropentacyclo[5.3.0.0^{2,6}.0^{3,10}.0^{4,8}]decane-3-carbamate (10).**[7] To a solution of **9** (0.40 g, 1.5 mmol) in *tert*-butyl alcohol (15 mL) was added triethylamine (0.153 g, 1.5 mmol) and diphenylphosphoryl azide (0.421 g, 1.5 mmol). The resulting mixture was refluxed for 12 h, at which time the reaction

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mixture was concentrated in vacuo. The residue was digested with hot hexane. The hexane was evaporated, leaving the crude urethane which was recrystallized from ethyl acetate–hexane mixed solvent to afford pure **10**: 0.32 g, 57%; mp 133–134 °C; ^{1}H NMR ($CDCl_3$) δ 1.3 (s, 9 H), 1.51 (*AB*, J_{AB} = 11 Hz, 1 H), 2.26 (*AB*, J_{AB} = 11 Hz, 1 H), 2.9–3.7 (m, 7 H), 5.1 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 28.34 (q), 35.29 (d), 37.67 (t), 42.22 (d), 43.57 (d), 45.30 (d), 45.96 (d), 47.31 (d) 58.14 (d), 67.14 (s), 80.20 (s), 128.36 (s), 154.14 (s); IR (KBr) 3330 (s), 2980 (m), 1660 (vs), 1550 (vs), 1360 (m), 1165 (s), 785 (m) cm^{-1}; mass spectrum (70 eV), *m/e* (relative intensity) (no molecular ion), 235.15 (3.8), 189.05 (10.0), 115.05 (9.1), 66.05 (21.6), 64.95 (10.0), 59.05 (32.9), 57.05 (100.0), 56.05 (15.9), 55.05 (11.1), 53.05 (12.0), 50.95 (15.4), 43.95 (31.2), 43.05 (11.5), 41.05 (59.3).

Anal. Calcd for $C_{15}H_{19}N_3O_6$: C, 53.41; H, 5.68. Found: C, 53.67; H, 5.55.

3,5,5-Trinitropentacyclo[5.3.0.0^{2,6}.0^{3,10}.0^{4,8}]decane (1). Urethane **10** (100 mg, 0.297 mmol) was dissolved in dry methanol (10 mL). This solution was cooled via external application of a dry ice–acetone bath, and dry hydrogen chloride gas was bubbled through the solution for 3 h. The reaction mixture was then allowed to warm to ambient temperature and was stirred overnight. The reaction mixture was then concentrated in vacuo, and the residue was washed with hexane. A colorless microcrystalline solid, 5,5-dinitropentacyclo[5.3.0.0^{2,6}.0^{3,10}.0^{4,8}]decyl-3-amine hydrochloride, (**11**, 73 mg, 90%), mp >200 °C, was thereby obtained.

Amine salt **11** (250 mg, 0.91 mmol) was dissolved in water (10 mL), and the resulting aqueous solution was extracted with ether to remove organic contaminants. The aqueous solution was rendered basic by careful addition of excess saturated aqueous sodium bicarbonate solution. The resulting turbid mixture was extracted with ether (20 mL). The ether extract was washed successively with water and with brine, dried (anhydrous sodium sulfate), and filtered, and the filtrate was concentrated in vacuo. The free amine, **12** (210 mg, 82%), was thereby obtained.

A solution of amine **12** (210 mg, 0.886 mmol) in dichloroethane (2 mL) was added dropwise to a refluxing solution of *m*-chloroperbenzoic acid (611 mg, 3.54 mmol) in dichloroethane (10 mL). After all of the amine had been added, refluxing was continued for an additional 3 h. The reaction mixture was then cooled to room temperature, and methylene chloride was added. The resulting mixture was washed sequentially with dilute aqueous sodium bicarbonate solution, with water, and with brine, dried (anhydrous sodium sulfate), and filtered, and the filtrate was concentrated in vacuo. The residue was recrystallized from ethyl acetate–hexane mixed solvent, furnishing **1** (150 mg, 61.3%) as a colorless microcrystalline solid, mp 191–192 °C: ^{1}H NMR ($CDCl_3$) δ 1.70 (*AB*, J_{AB} = 9.5 Hz, 1 H), 2.29 (*AB*, J_{AB} = 9.5 Hz, 1 H), 2.9–3.4 (m, 3 H), 3.45–3.68 (m, 1 H), 3.7–3.9 (m, 2 H), 4.0–4.2 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 35.23 (d), 37.99 (t), 42.43 (d), 43.19 (d), 44.93 (d), 46.66 (d), 50.72 (d), 58.79 (d), 92.11 (s), 126.24 (s); IR (KBr) 3000 (m), 1550 (vs), 1510 (vs), 1350 (vs), 1320 (s) cm^{-1}; mass spectrum (70 eV), *m/e* (relative intensity) (no molecular ion), 175.05 (38.1), 144.05 (20.2), 129.05 (26.4), 128.05 (63.8), 127.05 (32.7), 117.05 (40.6), 116.05 (53.1), 115.05 (100.0), 105.05 (31.9), 103.05 (31.1), 102.05 (27.5), 91.05 (61.9), 79.05 (33.2), 78.05 (24.8), 77.05 (59.7), 66.05 (52.3), 65.05 (41.7), 54.95 (42.2), 51.05 (63.8).

Anal. Calcd for $C_{10}H_9N_3O_6$: C, 44.95; H, 3.40. Found: C, 45.08; H, 3.59.

Acknowledgment. Financial[13] support of our study by the United States Army Armament, Munitions, and Chemical Command, the Air Force Office of Scientific Research, The Robert A. Welch Foundation (Grant B-963), and the North Texas State University Faculty Research Committee is gratefully acknowledged.

Registry No. 1, 89773-39-7; **3**, 89773-40-0; **4**, 69580-37-6; **5**, 69580-38-7; **6** (isomer 1), 89773-41-1; **6** (isomer 2), 89773-42-2; **7** (isomer 1), 89773-43-3; **7** (isomer 2), 89826-71-1; **8** (isomer 1), 89773-44-4; **8** (isomer 2), 89826-72-2; **9**, 89773-45-5; **10**, 89773-46-6; **11**, 89773-47-7; **12**, 89773-48-8.

(13) Research sponsored by Air Force Office of Scientific Research, Air Force Systems Command, USAF, under Grant No. AFOSR-84-0085.

A Novel Electrogenerated Base. Alkylation of Methyl Arylacetates at the α-Methylene Group[1]

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Received September 27, 1983

The formation of basic species from probasic compounds (PB) under the conditions of electroreduction has attracted much attention from mechanistic and synthetic points of view, though only limited types of PBs such as azobenzenes,[2-5] α,β-unsaturated compounds,[6-8] and oxygen[9,10] have been reported in the latter case so far. We have previously reported that a novel electrogenerated base (EGB, **2**) is formed by the cathodic reduction of 2-pyrrolidone (**1**) in DMF (Scheme I), and **2** is effective in promoting the aldol condensation of aldehydes,[11] the Stevens rearrangement,[12] and the condensation of chloroform with aliphatic aldehydes.[13]

In this paper, we report that **2** is also effective as a catalyst to promote α-alkylation of methyl arylacetates leading to the synthesis of some α-alkylarylacetic acids which possess high antiinflammatory and analgesic activities.[14,15]

Although one of the most convenient methods for the synthesis of α-alkylarylacetic acids seems to be the direct alkylation at the α-position of alkyl arylacetates **3**, the exclusive α-monoalkylation of **3** is not easily achievable under the reaction conditions with the usual bases. For example, α-monoethylation of ethyl phenylacetate in the presence of potassium[16] gave the desired product only in 35% yield, and α-methylation of alkyl phenylacetate using sodium amide[17] or sodium hydride as a base gave a mixture of alkyl 2-phenylpropanoate and alkyl 2-methyl-2-phenylpropanoate in 69–90% yield.[18] Because of the

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(18) The separation of these products is not always easy.

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